A high efficient method for introducing reactive amines onto carbon fiber surfaces using hexachlorocyclophosphazene as a new coupling agent

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ABSTRACT

To improve the interfacial properties of carbon fiber (CF) reinforced composites, an innovative and simple functionalized strategy has been proposed by grafting 4,4′-oxydianiline (ODA) onto carbon fiber surface using hexachlorocyclophosphazene (HCCP) as a novel coupling agent at mild reaction conditions. The chemical composition of the CF surface was confirmed by X-ray photoelectron spectra (XPS). The surface topography and surface energy of CF were examined by atomic force microscope (AFM) and dynamic contact angle tests (DCA), respectively. The interfacial shear strength (IFSS) of CF reinforced composites was studied by microbond test. The tensile strength of CF was measured by single filament tensile test. After functionalization treatment, the grafted amine groups on the fiber surface enhanced the surface wettability of modified CF and formed strong chemical bonding between fiber and matrix, improving the interfacial adhesion strength of composites. The interfacial shear strength of modified CF reinforced composites increased by 71.2% compared with that of desized CF. The interfacial enhancement mechanism was also discussed in detail. Moreover, the modified CF almost kept the original mechanical properties after functionalization.

1. Introduction

Carbon fibers (CF) reinforced composites with their favorable specific strength and specific stiffness are widely used in many cutting-edge fields, such as aerospace and automotive industries [1–4]. However, the interfacial performance of carbon fiber reinforced composites is weak due to the poor wettability and adhesion strength between carbon fiber and matrix, which is caused by the non-polar and inactive surfaces of carbon fibers. The poor interfacial properties of composites have a negative effect on overall mechanical properties [5–10]. Therefore, in the past decades, many research efforts have been made to increase the polarity and activity of carbon fibers, and thus improve the interfacial adhesion of the resulting composites. A variety of surface treatments of CF, such as electrochemical method [11], plasma treatment [12,13], coating [14–17] and chemical grafting [18–24] have been successfully achieved.

Chemical grafting coupling agents is one of most effective strategies to introduce active groups onto carbon fiber surfaces, enhancing the wettability and reactivity, and finally resulting in good interfacial properties of composites. Besides that, on the basis of these active amines, some nanoscaled carbon reinforcements (such as carbon nanotube and graphene oxide) can be introduced onto the fiber surface to prepare the hybrid reinforcements by chemical grafting [21–24]. Various diamines or polyamines, such as ethylene diamine [9,20,21], 1,3-propodiamine [22], 1,4-cyclohexanediamine [23] and tetraethylenepentamine [18,19] are good candidates for coupling agents. In these proposed methods, forming amide is the key step. However, it is difficult for amines to react with carboxylic groups on the CF surfaces forming amide bonds under a mild condition [18,19]. The reaction condition is always harsh [18,19]. The carboxyl groups have to previously convert into highly reactive acyl chlorides in a corrosive media and with a long reaction time [20,23]. So these modification procedures are rather complicate. Recently, some peptide coupling reagents are utilized to activate the condensation between the amino and carboxylic groups [9,21,22]. Unfortunately, these peptide coupling reagents are expensive. Moreover, the grafting density of amines is not very high. On the one hand, those diamine coupling agents only have two amine groups in each molecule. On the other hand, only

one part of the carboxyl groups (about 50%) on the fiber surface can react with amine groups forming amide bonds [18]. As detailed in above references, only one amine group is introduced onto the CF surface for each carboxyl group consumed during the grafting process [20–23]. Therefore, the quantity of amine groups grafted onto fiber surface is limited.

Nowadays many researchers have tried to develop novel coupling agents with multiple functional groups (such as octaglycidyldimethylsilyl POSS [9] and PAMAM dendrimer [8,24,25]) to improve the interfacial adhesion strength of composites by introducing more active groups on the CF surfaces. However, these methods are still directly or indirectly based on the formation of amide bond between the amine and carboxyl groups. Some issues in the amide formation step mentioned above cannot be avoided.

Hexachlorocyclophosphazene (HCCP, $N_3P_3Cl_6$) is a kind of inorganic ring material containing alternating phosphorus and nitrogen atoms. HCCP has a robust heterocyclic ring with six remarkably active P—Cl groups that can react with many nucleophiles, such as amines [26–29], alcoholic groups [30–32], phenolic groups [33–35], giving rise to several different classes of multifunctional cyclophosphazenes. Their physical and chemical properties can easily be tailored via substitution with appropriate functional groups. This important feature enables HCCP to functionalize the surfaces of solid materials [36–40]. In our previous work [41], a layer of amine-capped cross-linked polyphosphazenes was grafted onto CF surfaces through in-situ polycondensation between HCCP and 4,4′-oxydianiline (ODA), introducing a great amount of active amines onto the fiber surfaces, and finally improving the interfacial shear strength of carbon fiber composites.

In the present work, we propose a simple, efficient and alternative surface treatment method to functionalize carbon fiber surfaces with plenty of active amines by grafting 4,4′-oxydianiline (ODA), using HCCP as a novel coupling agent, under mild reaction conditions. The functionalized fibers possess a layer of amines (at molecule level) linked to fiber surfaces, which are more suitable to be further chemically reacted with resin matrix, thus forming a layer of interface with the same or similar composition of matrix, improving the wettability between fibers and resin matrix, and diminishing the defect at the interface. Being different from the previous chemical modification of CF surface [18–25], the present method is based on phenolic hydroxyl rather than carboxyl groups on the fiber surfaces. For our modification strategy, to be specific, first, the carbon fiber was oxidized with concentrated nitric acid in a shorter time to generate more free phenolic hydroxyl instead of carboxyl groups. Second, HCCP was grafted onto CF surfaces via the formation of strong C—O—P covalent bond between active P—Cl and phenolic hydroxyl groups. Finally, the rest of highly reactive P—Cl groups on CF surfaces were substituted by 4,4′-oxydianiline (ODA). So, it was expected that the quantity and density of amine groups on the functionalized CF would be much higher than that of the modified CF through the methods based on amide formation [18–25]. It was also expected to bring a new hope for the further improvement in interfacial adhesion property. The surface properties of functionalized carbon fibers were characterized by X-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM) and dynamic contact angle tests (DCA). The tensile strength of carbon fiber was measured by single filament tensile test. The interfacial shear strength between carbon fiber and matrix was studied by microbond test.

2. Experimental

2.1. Materials

T700S carbon fibers (12 K, 1.80 g/cm^3), with an average diameter of 7 μm, was purchased from Toray Industries, Inc., Japan. The epoxy resin matrix AEP 312 A and the curing agent AEP 312 B were purchased from Ningbo Ocean Chemical New Materials Technology Co., Ltd. (Ningbo, China). AEP 312 A and AEP 312 B were used at a weight ratio of 2:1. 4,4′-oxydianiline (ODA), tetrahydrofuran (THF) and triethylamine (TEA) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Anhydrous acetonitrile was obtained from Aladdin Industrial Inc., American. Hexachlorocyclophosphazene (HCCP) was purchased from Zibo Lanyin Chemical Co. Ltd., China. Concentrated nitric acid (60%) was purchased from Shanghai Chemical Factory, China. Anhydrous triethylamine (TEA) was prepared by refluxing in the presence of phthalic anhydride and distilling under the protection of nitrogen. Anhydrous tetrahydrofuran was prepared by distillation from sodium/benzophenone under the protection of nitrogen.

2.2. Grafting procedure of carbon fibers

The carbon fibers were extracted with acetone for 48 h to remove the sizing agent, and named CF. Then the desized fibers were oxidized in concentrated nitric acid (HNO$_3$) at 100 °C for 2 h to introduce polar groups (such as hydroxyl and carboxyl groups). Subsequently, the oxidized fibers were taken out and washed several times with deionized water until pH ∼ 7 and then dried at 80 °C under vacuum, named CFO. The oxidized fibers were dipped into the uniform solution of 0.4 g HCCP and 5 mL of triethylamine in 50 mL of anhydrous acetonitrile, and were kept at 50 °C for 24 h, obtaining the HCCP grafted fibers, named CFO–HCCP. CFO–HCCP fibers were washed by anhydrous THF and acetonitrile for 2 cycles, respectively, and then kept stirring in anhydrous acetonitrile for 1 h. And then CFO–HCCP fibers were immediately put into the uniform solution of 0.4 g ODA and 5 mL of TEA in 40 mL of anhydrous acetonitrile, reacting at 50 °C for 24 h, obtaining the ODA functionalized carbon fibers, named CFO-HCCP-ODA. The functionalized fibers were washed by anhydrous THF and acetonitrile for 2 cycles, respectively, removing the ODA residue and byproduct triethylamine hydrochloride. All reactions were carried out under a dry nitrogen atmosphere. The schematic of grafting procedures is illustrated in Fig. 1.

2.3. Characterization

The chemical compositions of carbon fiber surfaces were studied by X-ray photoelectron spectroscopy (XPS) using a Axis Ultra XPS instrument (Shimadzu, Japan) equipped with a monochromatic Al $K\alpha$ radiation (1486.6 eV). The binding energies were calibrated by referencing to C1s peak at 284.8 eV. The XPS CASA software was used for data analysis.

The surface topographies of carbon fibers were observed by a DI Multimode V scanning probe microscope (Dimension 3100V, Veeco, USA) using tapping mode at ambient condition. The surface roughness of carbon fiber (R_a) was obtained in an area of 4 μm × 4 μm.

The surface wettability of carbon fibers were evaluated by a Dynamic Contact Angle Meter and Tensiometer (DCAT 21, DataPhysics, Germany). Referring to Song's work [42], deionized water (γ = 72.8 mN/m, γ^d = 21.8 mN/m, γ^p = 51.0 mN/m) and ethylene glycol (γ = 48.3 mN/m, γ^d = 29.3 mN/m, γ^p = 19.0 mN/m) were selected as testing liquids. The advancing contact angle (θ) was determined from the mass change during immersion of the fiber into testing liquids using Wilhelmy equation:

$$\cos \theta = \frac{mg}{\pi d_f \gamma_l} \tag{1}$$

where d_f is the fiber diameter, g is the gravitational acceleration, and γ_l is the surface energy of the test liquid.
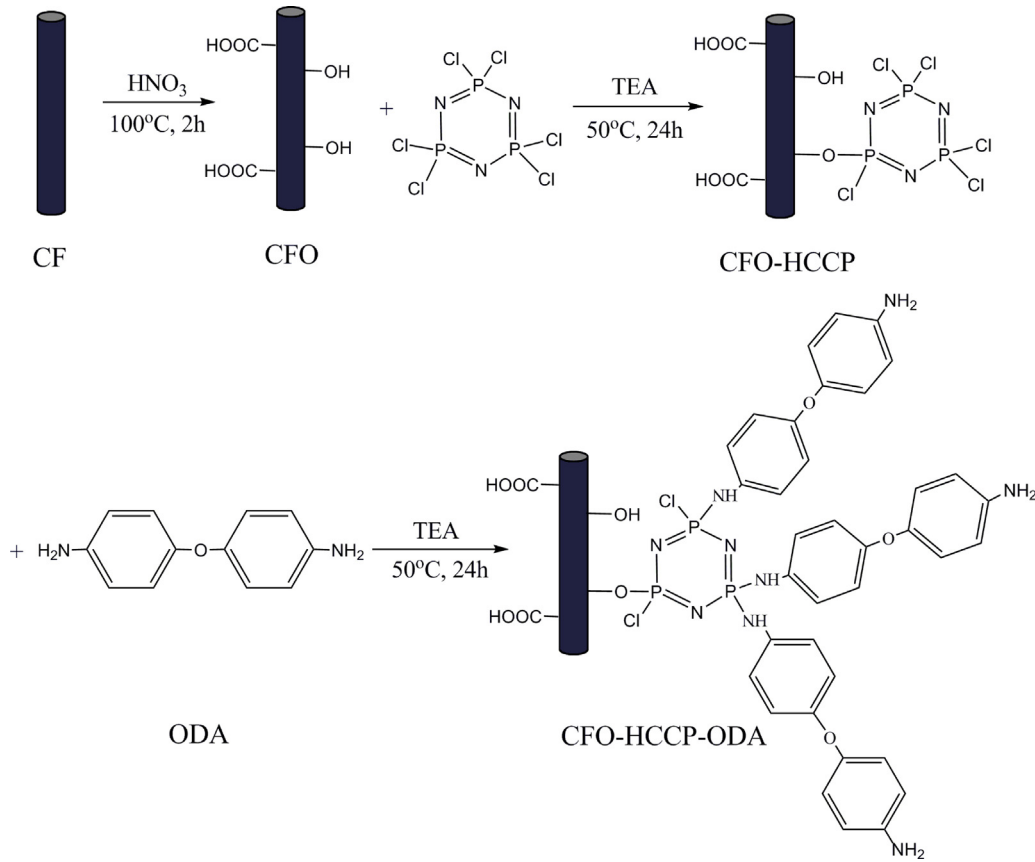
Fig. 1. The schematic of grafting procedure.

By using the measured contact angles and two testing liquids with known surface tension components, the dispersive and polar components of carbon fiber samples were calculated according to Owens–Wendt method as described in Eqs. (2) and (3).

$$\gamma_l \left(1 + \cos\ \theta\right) = 2\sqrt{\gamma_l^d \gamma_f^d} + 2\sqrt{\gamma_l^p \gamma_f^p} \qquad (2)$$

$$\gamma_f = \gamma_f^d + \gamma_f^p \qquad (3)$$

where γ is the surface tension, γ^d is the dispersive component, γ^p is the polar component. The subscript l and f means the testing liquid and carbon fibers, respectively. Each measurement was repeated 5 times and the results were averaged.

The tensile strengths of carbon fibers were measured by a XQ-1 tensile testing machine (Dong Hua University, Shanghai, China) at a cross-head speed of 5 mm/min [43]. The gauge length was 20 mm. At least 30 filament samples were tested for each case, and the average value was taken as the test result.

The interfacial shear strength (IFSS) was adopted to quantify the interfacial property between carbon fibers and matrix [14]. The schematic of microbond test is illustrated in Fig. 2. A carbon fiber monofilament was fastened to a paperboard with dimension of 26 mm × 58 mm using adhesive tape. Some resin microdroplets were applied to the monofilament using a steel needle, obtaining the single fiber composites (see Fig. 2a). The specimens were cured at 80 °C for 2 h and then 100 °C for 2 h. Microbond tests were conducted employing the interfacial evaluation equipment (MODEL HM410, Tohei Sanyon, Japan). The frame together with fiber was moved at a crosshead displacement rate of 1.0 μm/s. The microdroplets with embedded fiber length around 80.0 μm were chosen and debonded by fixture (see Fig. 2b). More specifically, the chosen embedded fiber lengths were 78.1 ± 5.0 μm, 79.6 ± 5.7 μm and

78.4 ± 4.4 μm for CF, CFO and CFO–HCCP–ODA fibers, respectively. The debonding load was recorded by computer. The IFSS was calculated as the following equation [14]:
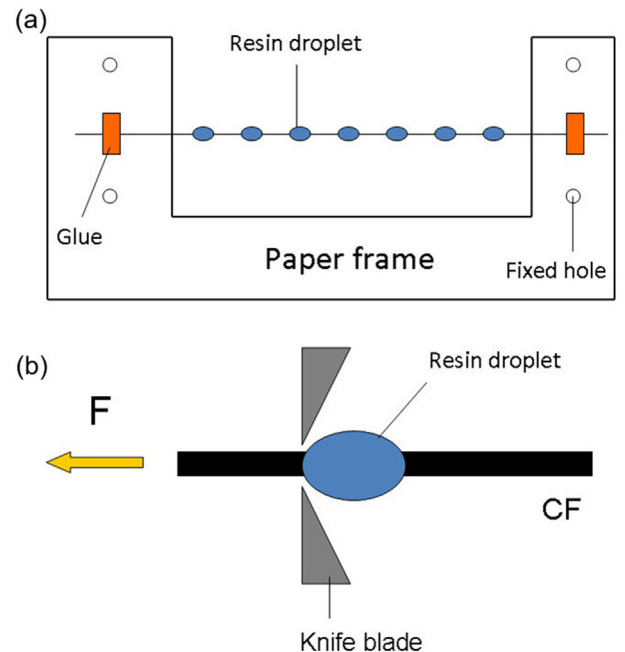
$$\tau = \frac{F_{max}}{\pi d_f L_e} \qquad (4)$$

Fig. 2. The schematic of single fiber microbond test.

where τ is the interfacial shear strength, F_{max} is the maximum tensile force, d_f is the diameter of the carbon fiber, and L_e is the embedded length of the fiber. At least 30 valid data were collected for every group of specimens and then averaged.

The surface morphologies of the carbon fibers debonding from matrix were obtained employing a field emission scanning electron microscope (S-4800, Hitachi, Japan), operating at an accelerating voltage of 4 kV. The samples were sputter coated with Pt.

3. Result and discussion

3.1. Description of surface functionalization strategy

The strategy devised for surface functionalization of carbon fibers is based on the exploitation of HCCP, which is utilized as a highly reactive and efficient coupling agent to bond carbon fibers and diamine compounds. In this study, 4,4′-oxydianiline (ODA) is chosen as a sample, which is widely used as curing agents in the composite material field. And a two-step procedure is employed to graft ODA onto fiber surface, as shown in Fig. 1. In the first step, HCCP was fixed onto CFO surface through the reaction between the active P—Cl and hydroxyl groups instead of carboxyl groups, forming strong covalent C—O—P bonds. The chemical reactivity and quantity of active sites of carbon fiber can be remarkably enhanced. Because multiple P—Cl groups were introduced for each hydroxyl group consumed. In the second step, ODA molecules were grafted onto the carbon fiber surfaces through nucleophilic substitution reaction between amine groups of ODA and the P–Cl groups on the CFO–HCCP surfaces, obtaining CFO–HCCP–ODA fibers. In the two-step grafting process, a weakly alkaline triethylamine (TEA) was used as catalyst to accelerate the reaction and trap byproduct HCl. It is expected that the wettability and interfacial adhesion strength between carbon fibers and matrix can be improved due to the abundant amine groups grafted on the fiber surfaces. Futhermore, these active amines have a potential to connect nanoscaled carbon reinforcements onto the fiber surfaces with higher density, thereby forming better multi-scale reinforcements. And in our lab, the research efforts are focusing on grafting graphene oxides onto CFO–HCCP–ODA surfaces now. In addition, the reaction conditions in the whole process are mild, which can prevent to reduce the original mechanical properties of carbon fibers.

### 3.2. Surface chemical compositions of carbon fibers

In this work, CF was prepared by soxhlet extraction with acetone to remove epoxy sizing from the commercial T700 fibers. To verify the epoxy sizing removing by acetone, XPS survey scans were performed to detect the surface elemental compositions of T700 and CF, and the results are shown in Supporting Information (Figs. S1 and S2, Tables S1 and S2). XPS results indicate that most of epoxy sizing on the fiber surface was cleaned by acetone. Though it is difficult to remove the sizing completely by the mild method, the little residual sizing had no negative effect on the next modification and the final conclusion. Because the little residual sizing, or a thin layer of the weakly bonded materials on the fiber surfaces can be further cleaned by concentrated nitric acid in the oxidation treatment.

To verify the chemical reaction of the grafting procedures, XPS survey scans were performed to detect the surface elemental compositions of carbon fibers, the results are summarized in Table 1 and shown in Fig. 3. As shown in Fig. 3a and b, in the XPS wide scan spectra of the desized fibers (CF) and oxidized fibers (CFO), three peaks centered around 284.8, 532.1 and 400.0 eV can be observed, which are assigned to C 1s, O 1s, and N 1s, respectively. The surface elements of CF is mainly composed of carbon, oxygen and insignificant amount of nitrogen. After oxidation treatment with HNO₃, the

Table 1
Surface element analysis of CF, CFO and CFO–HCCP–ODA.

Sample	Element content (at%)						
	C	O	N	P	Cl	N/P	Cl/P
CF	83.6	13.6	2.8	0	0	–	–
CFO	74.3	22.1	3.6	0	0	–	–
CFO–HCCP–ODA	61.6	27.6	8.1	2.1	0.6	3.9	0.3

carbon content decreased from 83.6% to 74.3%, and the oxygen content increased dramatically from 13.6% to 22.1%. Some of the carbon atoms on the fiber surface were converted to hydroxyl and carboxyl groups [21]. As presented in Fig. 3c, after grafting HCCP and ODA, besides C 1s, O 1s and N 1s peaks, two new peaks of Cl 2p at 200.7 eV and P 2p at 134.1 eV are found in the surfaces of CFO–HCCP–ODA.
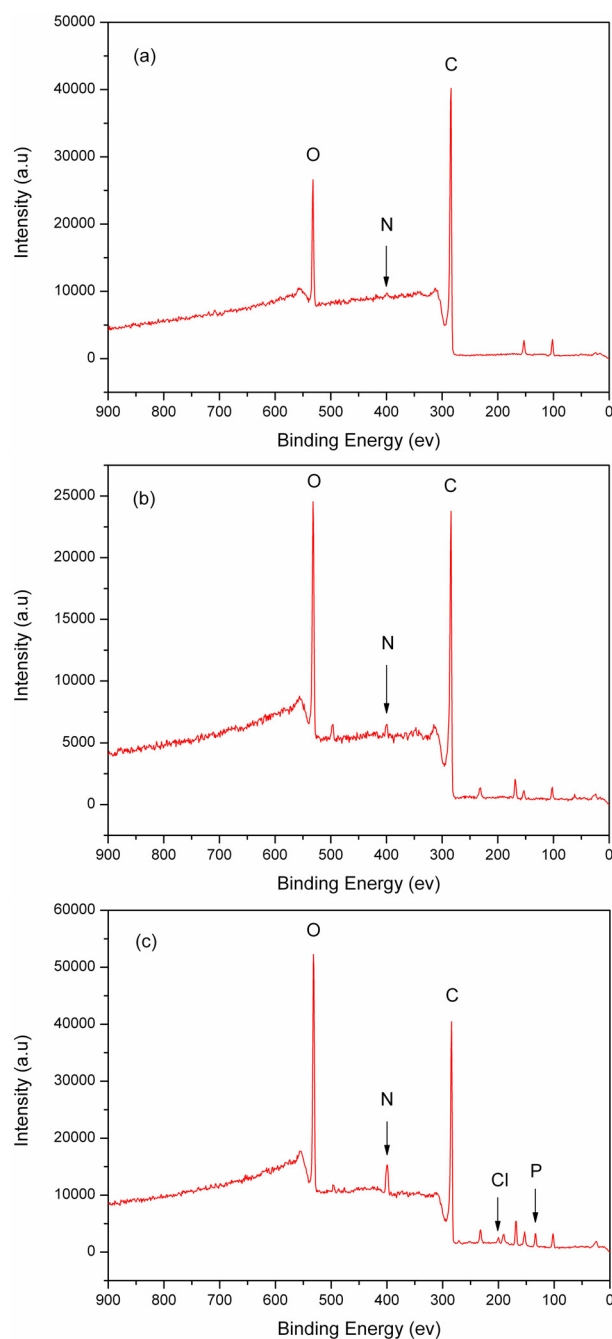
Fig. 3. XPS wide scan spectra of (a) CF, (b) CFO and (c) CFO–HCCP–ODA.

Table 2
Component peaks and attributions of N 1s curve fitting for CF, CFO and CFO–HCCP–ODA.

N peaks		Binding Energy (eV)	Attributions
CF	N1	400.5	Nitrogen heterocycles
CFO	N1	400.7	Nitrogen heterocycles
	N2	405.6	Nitro group ($-NO_2$)
CFO–HCCP–ODA	N1	398.1	Phosphazene ring (P$-$N$=$P)
	N2	399.5	Free amines of ODA (Ph$-NH_2$)
	N3	401.7	Protonated N (N^+)

Compared with CFO, the carbon content decreased significantly to 61.6%, and the nitrogen content increased obviously to 8.1%. In addition, the new peak of phosphorus was detected with a content of 2.1%. It is worth noting that surface atomic N/P ratio is 3.9. It is known that HCCP molecular only has a stoichiometric N/P ratio of 1. These findings imply that ODA was successfully grafted onto the fiber surfaces using HCCP as a coupling agent. Furthermore, in CFO–HCCP–ODA, the P 2p peak at 134.1 eV slightly lowering than that of the pure HCCP (134.6 eV) [44] also demonstrates that nucleophilic substitution reactions between P$-$Cl groups and phenolic hydroxyl on the CFO surface or/and amines of ODA were realized successfully [40]. Besides that, the presence of residual chlorines (0.6%) suggests that P$-$Cl groups of HCCP were not substituted completely by ODA. It may be due to the stereo-hindrance effect. Another possible reason for the presence of residual chlorines is that some byproduct HCl molecules were adsorbed on the fiber surfaces by the interaction with N of HCCP or/and ODA, forming the protonated nitrogens (N^+) [37].

Further information can be inferred by curve fitting of the N 1s spectra in Fig. 4. In the N 1s curve fitting of CF (see Fig. 4a), the only component centered at 400.5 eV is assigned to some nitrogen heterocycles originated from poly(acrylonitrile), which is the original materials of carbon fibers [45–47]. In the N 1s curve fitting of CFO (see Fig. 4b), the major component N1 centered at 400.7 eV is also assigned to nitrogen heterocycles originated from poly(acrylonitrile). The minor component N2 located at 405.6 eV is attributed to the nitro group ($-NO_2$), which was introduced during the oxidation treatment by nitric acid [46]. In the case of CFO-HCCP-ODA (see Fig. 4c), N 1s peak was fitted to 3 curves (N1, N2 and N3) with binding energy at 398.1, 399.5 and 401.7 eV, respectively. N1 (398.1 eV) is assigned to nitrogen of the phosphazene ring or chain (P$-$N$=$P) [37–40,44,48]; while N2 (399.5 eV) is reasonably attributed to the free amine groups (Ph$-NH_2$) of ODA molecules grafted on the carbon fiber surfaces [29]; N3 (401.7 eV) is due to protonated N (N^+) [37,47], which was caused by the interaction with hydrochloric acid, a byproduct in the grafting process. The component peaks and attribution of N 1s curve fitting for CF, CFO and CFO–HCCP–ODA fibers are summarized in Table 2. Based on the above XPS results, the conclusion can be draw that ODA was successfully grafted onto the carbon fiber surfaces using HCCP as a bridging agent, and a great amount of free amines were introduced onto the carbon fiber surfaces. These free amines can help to enhance the polarity and activity of the carbon fiber surfaces, thus resulting in good wettability and interfacial adhesion.

3.3. Surface topographies of carbon fibers

The surface topographies of desized, oxidized and modified carbon fibers were investigated using atomic force microscope with tapping mode. As shown in Fig. 5a and b, the surfaces of CF and CFO seem to be neat and smooth, with a roughness (R_a) of 6.1 and 5.4 nm, respectively. Compared with the CF, the roughness R_a
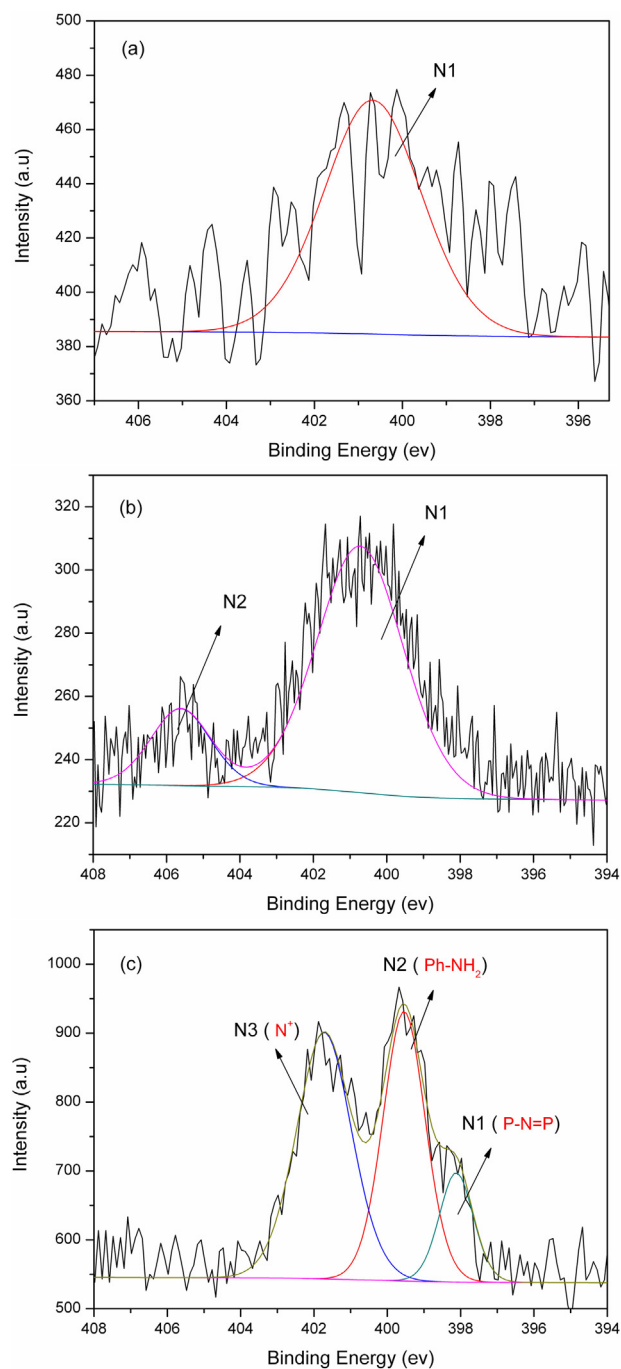
Fig. 4. XPS curve fitting of N 1s peak of (a) CF, (b) CFO and (c) CFO–HCCP–ODA.

of CFO slightly decreased to 5.4 nm, the similar phenomenon was reported in Refs. [41,47]. The slight decrease may arise from removing the little residual polymer sizing or a thin layer of the weakly bonded materials at apparent surface of carbon fiber by oxidation in a short time. In the case of CFO–HCCP–ODA (see Fig. 5c), after grafting HCCP and ODA molecules onto CFO, the surface became a bit rougher. With careful observation, a few of convex protrusions could be found on the surface. The roughness R_a slightly increased to 6.9 nm. However, in general, there is no significant difference in roughness among CF, CFO and CFO–HCCP–ODA fibers. The roughness of these carbon fibers are relatively low. Because the T700S carbon fibers have a inherent smooth and neat surfaces without any detectable groove along the longitudinal direction of fiber, unlike T300 carbon fibers [42].
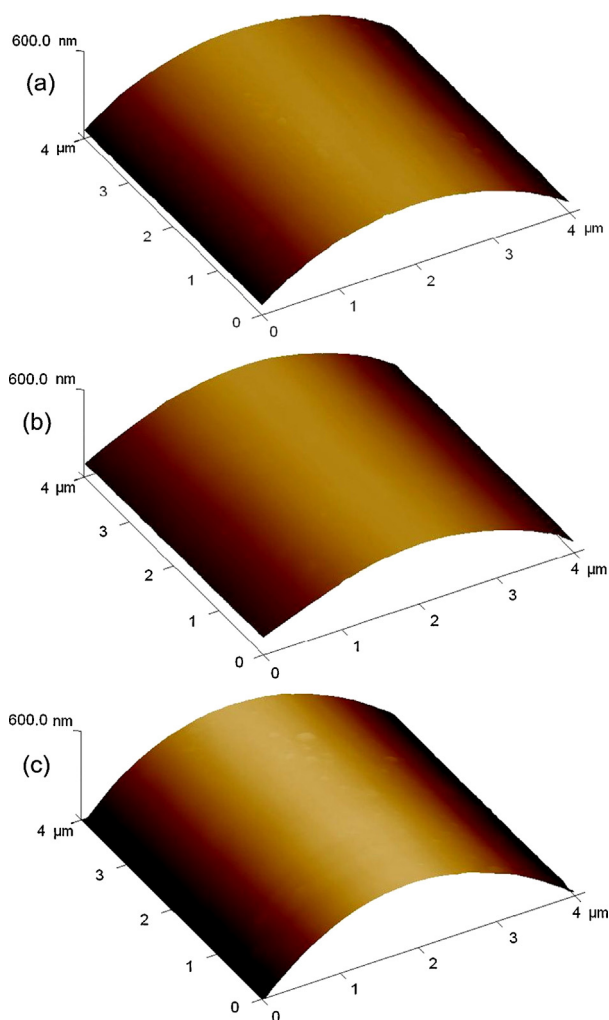
Fig. 5. AFM topography images of (a) CF, (b) CFO and (c) CFO–HCCP–ODA.

fibers decreased remarkably from 72.0° to 58.7° for water and from 72.3° to 62.8° for ethylene glycol. The surface energy increased to 54.8 mN/m, with a dispersive component of 0.3 mN/m and an enhanced polar component of 54.5 mN/m. Compared with CFO, the contact angles of CFO–HCCP–ODA increased slightly from 58.7° to 59.6° for water, and decreased slightly from 62.8° to 59.6° for ethylene glycol. The surface energy was 49.4 mN/m, with a dispersive component of 1.3 mN/m and a polar component of 48.1 mN/m. From the results, it can be found that the dispersive components of CF, CFO and CFO–HCCP–ODA fibers were all low, and there was no remarkable difference among them. The phenomenon is attributed to the intrinsic low roughness of T700S carbon fibers, which has been verified by AFM analysis above. The findings suggest that the obvious changes in surface energy of CF, CFO and CFO–HCCP–ODA are mainly due to the polar components. After oxidation treatment, the surface wettability of CFO increased dramatically. The introduced polar groups (such as carboxyl and hydroxyl groups) are responsible for the improvement of surface energy, especially its polar component. While after the further functionalization with HCCP and ODA, the surface energy and its polar component of CFO–HCCP–ODA slightly decreased. Theoretically, the polar amine groups could help to improve the polar component of surface energy. However, in the ODA molecule, the benzene ring segment is non-polar and its size is much bigger than amine groups. The characters make the ODA molecule weak-polar. And indeed, ODA is insoluble in water. In short, the ability of amine groups in enhancing the polar component of surface energy is weakened by non-polar benzene ring. On the other hand, the decrease of surface energy of CFO–HCCP–ODA compared with that of CFO may be caused by the stereo-hindrance effect. The molecular size of HCCP and ODA are much bigger than carboxyl and hydroxyl groups. Part of carboxyl and unreacted hydroxyl groups are covered and stopped from contacting with the testing liquids. Overall, in comparison with CFO, surface energy of CFO–HCCP–ODA had a slight decrease. However, compared with CF, surface energy of CFO–HCCP–ODA still had a dramatic increase, and the surface wettability of carbon fibers was enhanced significantly.

3.4. Dynamic contact angle and surface energy analysis

The performance of carbon fiber reinforced composite is related to the surface wettability of carbon fiber. Poor wettability usually results in a weak interfacial strength. Functionalization with HCCP and ODA on the fiber surface was expected to change the surface wettability of carbon fiber, which was evaluated by the contact angle (θ) and surface energy (γ). Deionized water and ethylene glycol, whose surface tension components were known, were used as testing liquids to measure the contact angle between testing liquids and single fibers. Surface energy (γ) is composed of two components, polar component (γ^p) and dispersive component (γ^d), which can be easily determined by solving the Eqs. (2) and (3). The results are summarized in Table 3. As shown in Table 3, the surface energy of desized fiber (CF) was 37.6 mN/m, with a dispersive component of 0.9 mN/m and a polar component of 36.7 mN/m. After oxidation with HNO$_3$, the contact angles of CFO

3.5. Tensile strength of single carbon fiber

In the present strategy, based on the hydroxyl groups of carbon fibers, the efficient grafting was achieved through an effortless process under mild conditions. A tensile testing machine was employed to evaluate the mechanical property, and a negligible change in tensile strength was observed (see Supporting information, Fig. S3). Tensile strength of CF, CFO and CFO–HCCP–ODA were 4.80, 4.69 and 4.75 GPa, respectively. Compared with CF, the single fiber tensile strength of CFO and CFO–HCCP–ODA had a insignificant decrease of 2.3% and 1.0%, respectively. The results indicate that the modified carbon fibers almost kept the original mechanical properties after functionalization with several steps. It is mainly due to the mild reaction conditions. Futhermore, it is notable that compared with CFO, the tensile strength of CFO–HCCP–ODA increased slightly from 4.69 to 4.75 GPa, by 1.3%. The result implies that grafting ODA onto the fiber surface, using HCCP as coupling

Table 3
Dynamic contact angles and surface energies of CF, CFO and CFO-HCCP-ODA.

Sample	Contact angle θ (°)		γ^d (mN/m)	γ^p (mN/m)	γ (mN/m)
	Water	Ethylene glycol			
CF	72.0 ± 5.3	72.3 ± 6.0	0.9	36.7	37.6
CFO	58.7 ± 5.1	62.8 ± 3.4	0.3	54.5	54.8
CFO–HCCP–ODA	59.6 ± 1.4	59.6 ± 2.6	1.3	48.1	49.4

agent, has a potential to protect the fibers from the defects caused from oxidation treatment by HNO_3.

3.6. Interfacial properties of carbon fiber/epoxy composites

Interfacial property is one of the most important performances for carbon fiber reinforced composites. The interfacial shear strengths (IFSS) of the composites were evaluated by microbond test. The results are showed in Fig. 6. IFSS values of CF, CFO and CFO–HCCP–ODA reinforced composites were 47.5, 56.6 and 81.3 MPa, respectively. Compared with desized CF, CFO increased IFSS of the composites by 19.2%, and CFO–HCCP–ODA significantly increased IFSS of the composites by 71.2%.

Generally, the mechanism of the improvement of interfacial shear strength is related to mechanical interlocking, surface wettability and chemical bonding between carbon fibers and matrix. While there is no obvious gap among the roughness of CF, CFO and
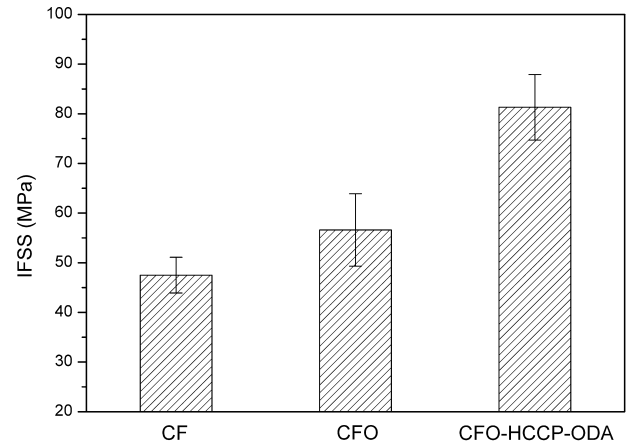

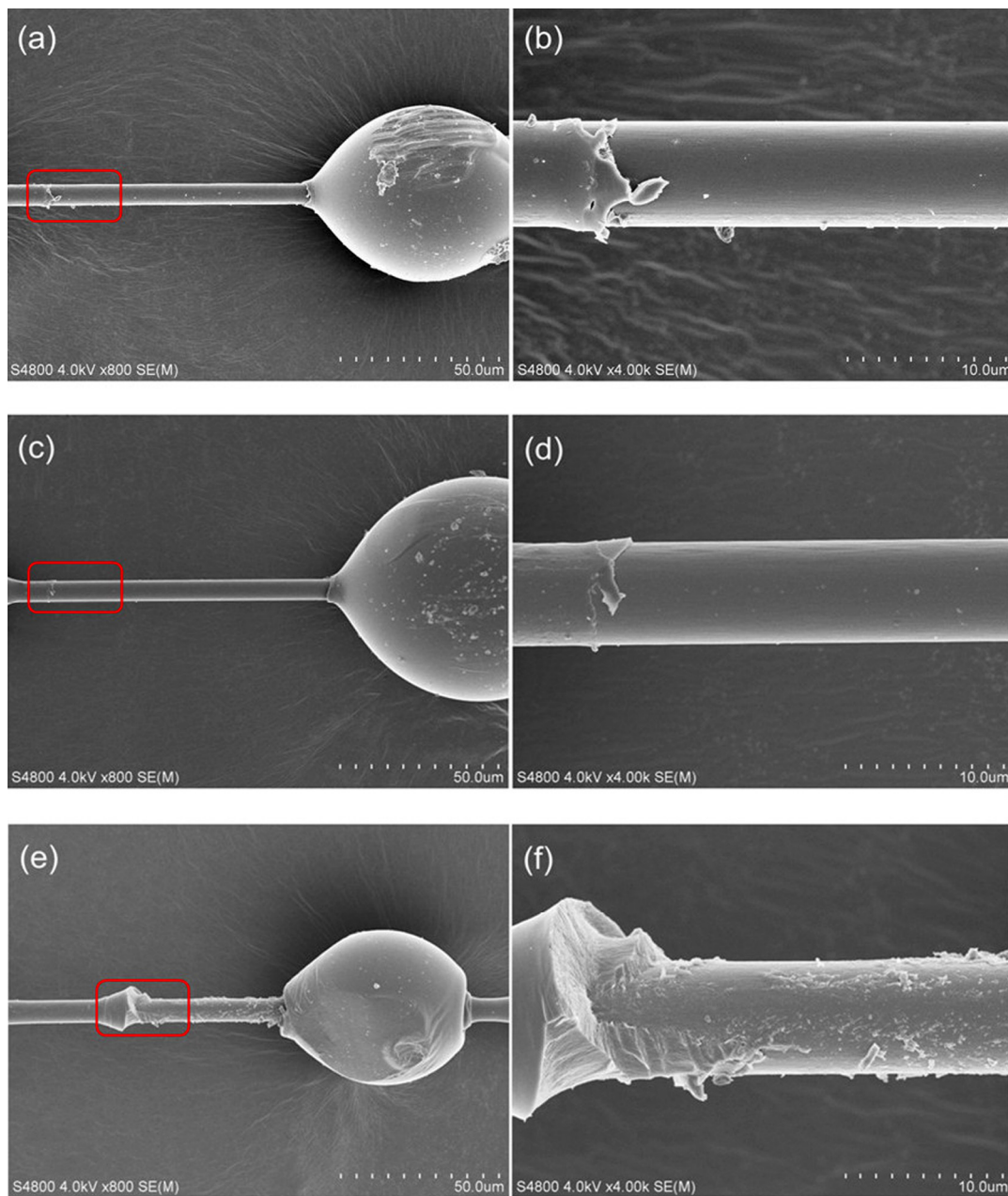**Fig. 6.** IFSS results of the composites reinforced by CF, CFO and CFO–HCCP–ODA.

Fig. 7. Surface morphologies of debonded samples: (a) and (b) CF, (c) and (d) CFO, (e) and (f) CFO–HCCP–ODA.

CFO–HCCP–ODA. The roughness of CFO was even slightly lower than that of CF. And the roughness of CFO–HCCP–ODA was only slightly higher than those of CF and CFO. The results indicate that the mechanical interlocking interaction is not the main factor responsible for the improvement of IFSS in this study.

From the surface energy data in Table 3, it can be seen that the surface energies of CFO and CFO–HCCP–ODA are higher than that of desized CF, which are beneficial to improve the surface wettability between fibers and matrix, and diminish the defect at the interface of composites, and avoid forming an interface of weak cohesion. Thus, the increased surface wettability between fibers and matrix led to the enhancement of the interfacial adhesion strength. Moreover, as shown in Table 3, the surface energy and polar component of CFO–HCCP–ODA are slightly lower than their corresponding parameters of CFO. However, the IFSS of CFO–HCCP–ODA reinforced composite is obviously higher than that of CFO. The results suggest that the grafted ODA is responsible for the dramatic improvement. In the CFO–HCCP–ODA reinforced composites, the grafted ODA can still work as a curing agent during the solidifying process. Namely, the grafted amine groups on the CFO–HCCP–ODA surface reacted with epoxy groups of matrix, forming strong chemical bonds between carbon fiber and matrix, which remarkably improved the interfacial adhesion strength of composites.

In order to verify the hypothesis, the surface morphologies of carbon fibers after debonding from matrix were examined by SEM. As shown in Fig. 7a–d, the debonded surfaces of CF and CFO are almost clean and smooth. This phenomenon suggests that the matrix completely detached from the fiber surface. The dominant fracture mechanism of the desized CF reinforced composites is interfacial debonding, which is due to the weak adhesion between fibers and matrix. For CFO fibers, though undergoing the oxidation treatment, introducing the polar groups onto the surfaces, and improving the surface wettability, the interfacial adhesion is not very strong. Because the chemical interaction between epoxy groups of matrix and polar groups of CFO is still insignificant. The main interaction between the matrix and carbon fiber surfaces is just the improved physical adsorption. After oxidation treatment, the enhanced surface wettability brings about a better physical adsorption, which can increase the interfacial adhesion strength to a certain extent. In comparison, for CFO–HCCP–ODA reinforced composite, a remarkably different fracture surface topography is shown in Fig. 7e and f. An amount of resin adhering on the fiber surface can be observed on the fractograph (see Fig. 7f). These results manifest that the interfacial adhesion strength between CFO–HCCP–ODA and epoxy matrix was so strong that the matrix could not be detached from the fiber surface, and the interfacial fracture started from the matrix. The above results also imply that chemical bonding played a key role in improving the interfacial properties of CFO–HCCP–ODA reinforced composite system, besides the enhanced surface wettability between fiber and matrix. In other words, the strong chemical bonds were created by the reaction of amines and epoxy groups between fiber surfaces and matrix in the solidifying process. Grafting ODA onto the carbon fiber surfaces using HCCP as a coupling agent enhanced the interfacial adhesion strength of the composites indeed.

4. Conclusion

In the present study, 4,4′-oxydianiline (ODA) was successfully grafted onto carbon fiber surfaces using hexachlorocyclophosphazene (HCCP) as a distinctive coupling agent, through a two-step substitution reaction route. A great amount of amine groups were introduced on the modified carbon fiber surfaces, which obviously helped to improve the surface wettability and facilitated to form strong chemical interactions between carbon fiber and matrix. Thus, the interfacial shear strength of CFO–HCCP–ODA composites increased significantly by 71.2% in comparison with that of desized CF composites. The interfacial fracture topographies of CFO–HCCP–ODA reinforced composites indicated that the strong chemical interactions played a dominant role in improving the interfacial properties. Moreover, the grafting reaction did not result in a significant change in tensile strength of carbon fibers. After functionalization with several steps, the modified carbon fibers almost kept the original mechanical properties.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2014.08.124.

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